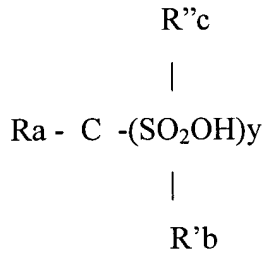
CLAIMS

1. A solution for copper electroplating which contains copper alkanesulfonate salts and free alkanesulfonic acids, wherein the free acid has a concentration from about 0.05 to about 2.50 M, and which is intended for the metallization of micron-sized dimensioned trenches or vias, through-holes and microvias.

2. The solution of claim 1 wherein the alkanesulfonic acid of the anionic portion of the copper salt and any free acid are introduced as an alkyl or aryl sulfonic acid of formula:



wherein a+b+c+y equals 4,

R, R' and R" are the same or different and each independently may be hydrogen, phenyl, Cl, F, Br, I, CF_3 or a lower alkyl group such as $(CH_2)n$ where n is from 1 to 7 and that is unsubstituted or substituted by oxygen, Cl, F, Br, I, CF_3, $-SO_2OH$.

3. The solution of claim 1 wherein the alkanesulfonic acid is derived from an alkyl monosulfonic acid, an alkyl polysulfonic acid or an aryl mono or polysulfonic acid.

4. The solution of claim 1 wherein the alkyl sulfonic acid is methanesulfonic, ethanesulfonic and propanesulfonic acids and the alkyl polysulfonic acids are methanedisulfonic acid, monochloromethanedisulfonic acid, dichloromethanedisulfonic acid, 1,1-ethanedisulfonic acid, 2-chloro-1,1-ethanedisulfonic acid, 1,2-dichloro-1,1-ethanedisulfonic acid, 1,1-propanedisulfonic acid, 3-chloro-1,1-propanedisulfonic acid,

1,2-ethylene disulfonic acid, 1,3-propylene disulfonic acid, trifluormethanesulfonic acid, butanesulfonic acid, perfluorobutanesulfonic acid, and pentanesulfonic acid and the aryl sulfonic acid are phenylsulfonic, phenolsulfonic and tolylsulfonic acids.

5. The solution of claim 1 wherein the alkanesulfonic acid is methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid or trifluormethanesulfonic acid.

6. The solution of claim 1 wherein the acid is a mixture of an alkanesulfonic acid with other acids.

7. The solution of claim 1 which contains a halogen ion from 0.01 to 200 mg/l.

8. The solution of claim 1 wherein no free acid is used.

9. The composition of claim 1 wherein the pH is between 0.05 to 7.5.

10. The solution of claim 1 wherein the copper salt is supplied as a mixture of a copper alkanesulfonate with other metal salts selected from metals in Group 1B, 2B, 3A, 3B, 4A, 4B, 5B, 6B, 7B, or 8 of the periodic table.

11. The composition of claim 1 wherein the suppressor additive is a high molecular weight polyether containing oxygen linkages.

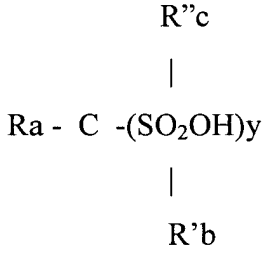
12. The composition of claim 1 wherein a sulfur-containing accelerator or brightener agent is at least about 0.05 to 100 mg per liter of the electroplating composition.

13. The composition of claim 1 wherein brightener agent is bis-sodium-sulfonopropyldisulfide.

14. The composition of claim 1 containing a nitrogen-containing leveler additive.

15. A process for the metallization of micron dimensioned trenches or vias or through-holes, wherein the process employs an electroplating solution containing copper alkanesulfonate salts and free alkanesulfonic acids, wherein the free acid has a concentration of from about 0.05 to about 3.50 M, and electric current is passed through the solution to electroplate copper unto a substrate.

16. The process of claim 15 wherein the alkanesulfonic acid of the anionic portion of the copper salt and any free acid are introduced as an alkyl or aryl sulfonic acid of formula:



wherein a+b+c+y equals 4,

R, R' and R" are the same or different and each independently may be hydrogen, phenyl, Cl, F, Br, I, CF_3 or a lower alkyl group such as $(CH_2)n$ where n is from 1 to 7 and that is unsubstituted or substituted by oxygen, Cl, F, Br, I, CF_3, $-SO_2OH$.

17. The process of claim 15 wherein the substrate is a semiconductor device or a printed circuit board with a thinly metallized surface containing micron or sub-micron dimensioned trenches, through-holes, or vias, and wherein the plating solution effectively plates copper into said trenches, through-holes or vias.

18. The process of claim 15 wherein direct current, pulsed current or periodic reverse current is used.

19. The process of claim 15 wherein a soluble or an insoluble or inert anode is used.

20. The process of claim 15 wherein the temperature of the copper electrolyte is between 20°C to 70°.

21. The process of claim 15 wherein the copper is pure copper or a copper alloy with a metal from Group 1B, 2B, 3A, 3B, 4A, 4B, 5B, 6B, 7B, or 8 of the periodic table.

22. The process of claim 15 wherein the substrate is a printed circuit board substrate or semiconductor with one or more vias or microvias or through-holes.

23. The process of claim 15 wherein the via or microvias or through-holes have an aspect ratio of about 1:1 and diameters of about 1 to 500 microns.

24. The process of claim 15 wherein copper is deposited to fill the one or more vias to provide a copper plate in the absence of dimples, overplate, voids or inclusions.

25. An article of manufacture comprising an electronic device substrate containing one or more through-hole, via, microvia or trench, the aperture walls having thereon an electrolytic copper deposit obtained from an electroplating composition from claim 1 that contains copper alkanesulfonate salts and free alkanesulfonic acids, a halogen ion, a suppressor additive, an accelerator additive, optionally a leveling additive and optionally a surfactant.

26. The article of claim 25 wherein the substrate is printed board substrate, a microchip module substrate, or a semiconductor chip substrate.

27. The article of claim 25 wherein the substrate comprises the one or more via, microvia or through-hole that has an aspect ratio of at least about 1:1 and diameters of at least about 1 microns to 500 microns.